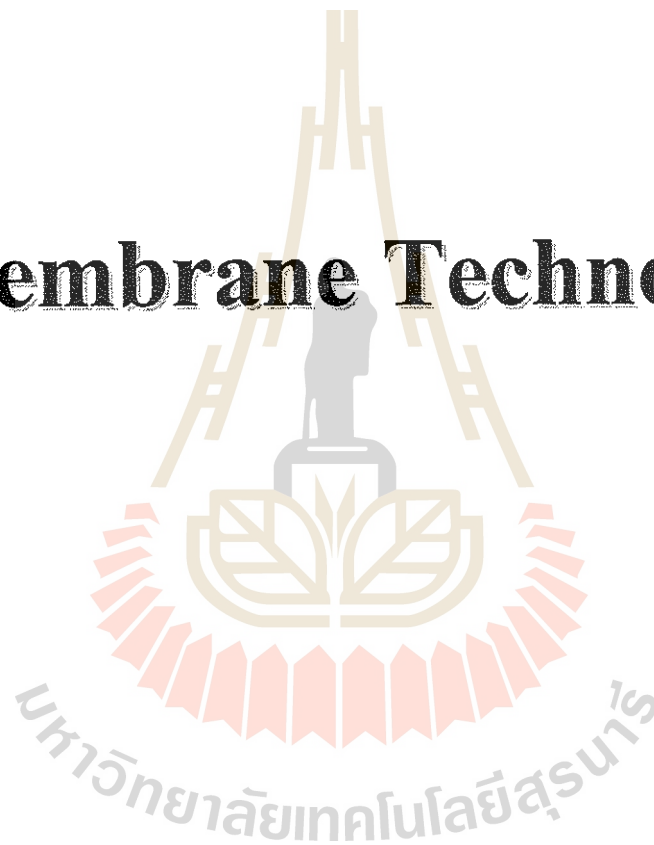


Agro-Industry Ph.D. Consortium

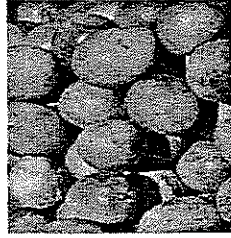
Seminar

Membrane Technology



Suranaree University of Technology
Nakhon Ratchasima

21 July 2004



Membrane Technologies for Fruit Juices Processing

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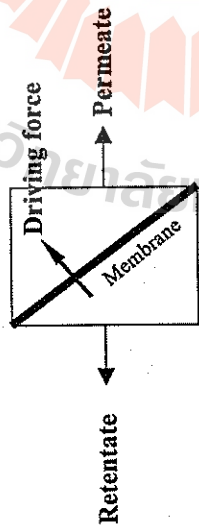
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Contents

- I. The membrane processes and their interest for fruit juice processing**
- II. Clarification / stabilization
MICROFILTRATION**
- III. Concentration
OSMOTIC EVAPORATION**
- IV. Deacidification
ELECTRODIALYSIS**
- V. Conclusion and perspectives**

Basic concepts of membrane processes

separation processes using a selective barrier: the membrane



Membrane: porous or not / organic or inorganic
plate, tubular or spiral-wound

Driving force: ΔP , ΔC , ΔT or ΔU

Operation characterized by:

retention: $1 - C_p / C_r$

performance: flux (J)

Tangential circulation of the fluids

Main membrane processes (food liquids)

Driving force	Process	Membrane type	Permeate	Separation by	Species separated	Main applications
ΔP	Microfiltration MF (1920)				microparticles	Clarification, sterilization
	Ultrafiltration UF (1930)	Porous, active	Liq.	Size, shape	macromolecule	Fractionation concentrat.
	Nanofiltration NF (1990)				molecules	Concentrat.
	Reverse osmosis RO (1960)	Non porous, active				Concentrat., desalting
ΔC	Direct osmosis DO (1980)	Non porous, active	Liq.			Concentrat.
	Pervaporation PV (1980)	Non porous, active	Gas	Thermo-dynamic activity	molecules	Concentrat., extraction
	Osmotic evaporation OE (1990)	Porous, contactor	Liq.			Concentrat.
ΔT	Membrane distillation MD (1980)	Porous, contactor	Gas	Thermo-dynamic activity	molecules	Concentrat., extraction
	Electrodialysis ED (1960)	Non porous, active	Liq.	Electrical charge	ions	Desalination, desalting

Driven-pressure membrane processes

Size selectivity
 ΔP as driving force
 Mass transfer in liquid phase

Process	Membrane	ΔP range	Species retained
MF	Porous 0.1 – 5 μm	0.1 – 3 bar	Cells, bacteria, yeasts, starch granules, oil globules, etc.
UF	Porous 5 – 100 nm	1 – 10 bar	Polysaccharides, proteins, tannins, virus, etc.
NF	Porous 1 – 5 nm	10 – 50 bar	Sugars, organic acids, polyphenols, aroma compounds, etc.
RO (hyper-filtration)	Non porous	10 – 100 bar	Salts

Fruit juices composition

Water
80-90 %

Soluble solids
Molecules (MW < 1 kDa)

sugars, organic acids, vitamins, polyphenols, aroma compounds, pigments, salts

Macromolecules (MW > 1 kDa)
polysaccharides, proteins, tannins

Insoluble solids
cells, cell walls, fibers, crystals, starch granules, microorganisms

Thermosensitive products

Main potentialities in fruit juices processing

Unit operation	Purpose	Membrane processes
Clarification	Removal of insoluble solids	MF / UF
Sterilization	Removal of microorganisms	MF / UF
Concentration	Removal of water	UF / RO / DO / PV / OE / MD
Deacidification	Removal of organic acids	ED

Economical context

> Expanded market

- Fruit juices market \approx 4 billions € / year
- Increasing exchanges
 - Pineapple + 4 % / year
 - Passionfruit + 4 %
 - Banana + 7 %
 - Mango, papaya + 25 %

> New market trends

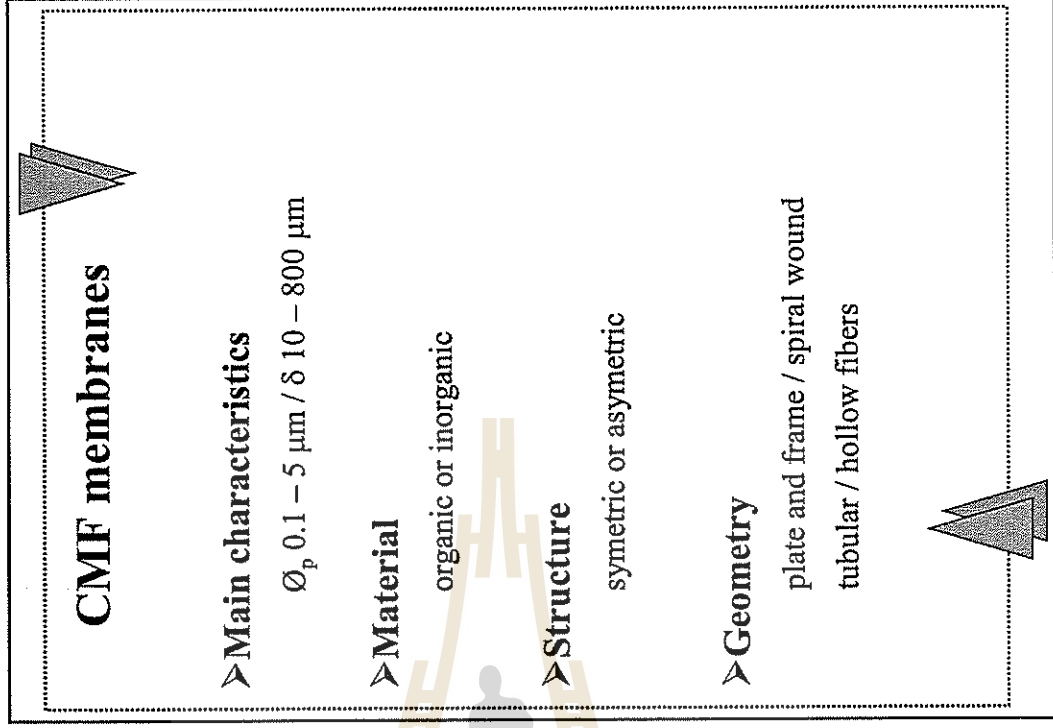
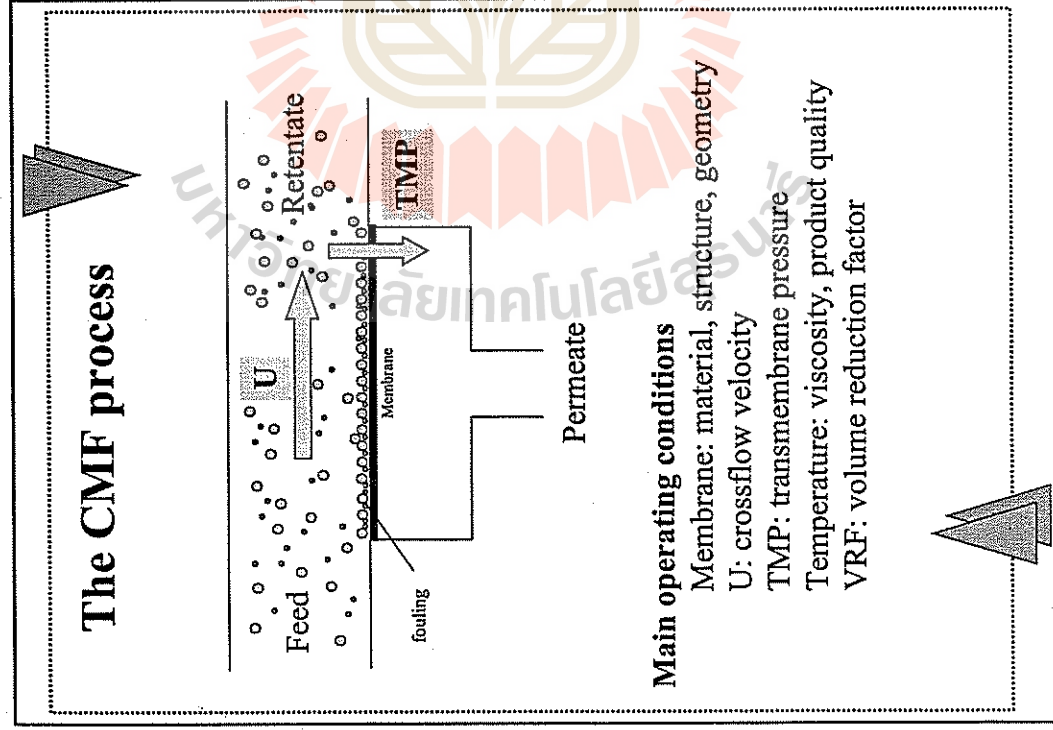
- Whole juices : nutritional and sensorial quality near the fresh fruits
- Juices for formulation (« intermediate food products »): diversification of the demand



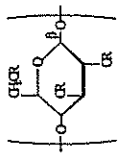
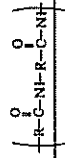
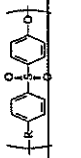
Emerging processes in the field of fruit juices

- **Crossflow microfiltration (CMF)**
clarification / cold stabilization
Industrial applications on temperate fruits (apple, grape)
development on tropical fruits
- **Reverse osmosis / Osmotic evaporation**
cold concentration
in development
- **Electrodialysis**
deacidification of acidic juices
very recent research works

Clarification / stabilization using crossflow microfiltration



Organic membranes

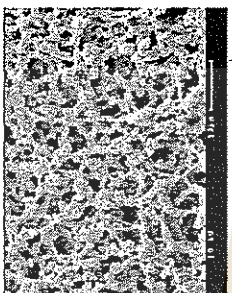
Polymer	Structure	Example	pH range	T _{max} (°C)	Cl _{max} (ppm)	Price
Cellulose derivatives	 $R: H, CO-CH_3$	Cell. acetate Cell. triacetate	3-8	40	10	--
Polyamides		Nylon Polyacrylamide	3-11	50	< 1	-
Polysulfone derivatives		Polysulfone Polyethersulfone	1-13	80	100	-

➤ **Cheap**

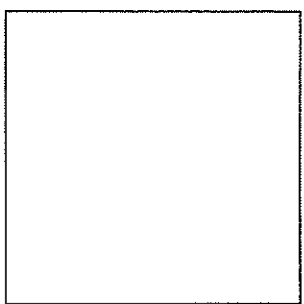
➤ **Bad physico-chemical resistance**
problem for cleaning / limited operating lifetime

Organic membranes

microscopic structure



Cellulose membrane
(network structure)



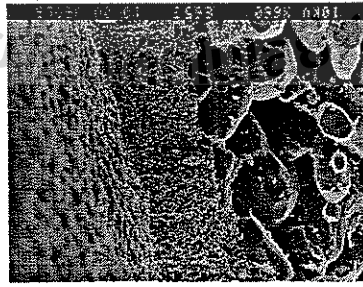
Polysulfone membrane
(tular-like structure)

Inorganic membranes

Ceramic membranes

Material

Al₂O₃ (alumina), ZrO₂ (zirconia), TiO₂ (titania)
Grains structure (baking at high temperature)



> High physico-chemical resistance

No problem for cleaning / sterilizable (Cl or T) / extended operating lifetime

> Expensive (x 10)

Membrane structure

> Symetric structure

easier to elaborate
high thickness => low flux



> Asymmetric structure

Thin-layer supported by a porous sublayer
Good mechanical resistance with high flux



Thin-layer

Support

Membrane geometry

Type	Organic	Mineral
Flat sheet (spacers 0.5-3 mm)		
Plate and frame	usual	rare
Spiral-wound	usual	no
Tubular		
Classic (ϕ 3-12 mm)	rare	usual single or multichannel
Hollow fibers (ϕ < 2 mm)	usual	no

Membranes geometry examples

The figure illustrates three types of membrane geometries with their respective materials and scale bars:

- Spiral-wound (organic):** A 3D diagram shows a spiral-wound module with labels for 'Feed Channel Membrane Space', 'Permeate Channels Space', and 'Feed Channel Membrane'. A photograph shows a physical module with two circular ports. A scale bar indicates 1 cm.
- Tubular multichannel (ceramic):** A photograph shows several ceramic tubular modules. A scale bar indicates 1 cm.
- Hollow fibers (organic):** A photograph shows a bundle of hollow fibers. A scale bar indicates 1 mm.

21 July 2004

Membranes selection for fruit juice processing

For pulpy juices (high viscosity)

- 1- tubular with high \emptyset
- 2- plate with large spacers

For cleaning / sterilization ability

- 1- ceramic
- 2- polysulfone derivatives

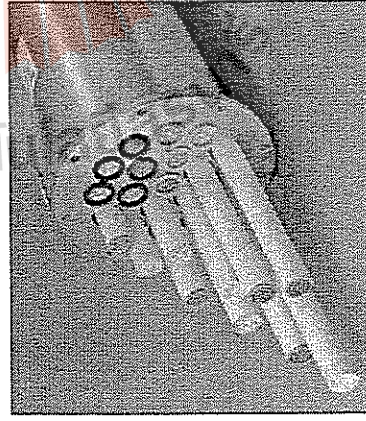
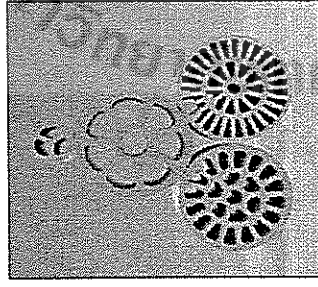
For investment cost

- 1- organic
- 2- ceramic

For retention and performance

To be tested on pilot plant
 $\emptyset_p \leq 0.2 \mu\text{m}$ for sterilization

Tubular multichannel: other profiles
(ceramic)



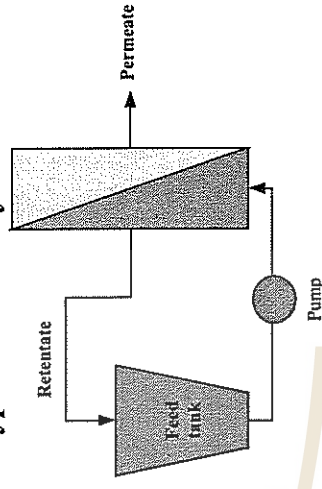
Operating conditions

- TMP** transmembrane pressure
to be optimized
0.1 – 4 bar
- U** crossflow velocity
increase flux, increase operating cost
 $1 - 10 \text{ m s}^{-1}$
- T** temperature
increase flux (\downarrow viscosity), decrease product quality
often $< 40^\circ\text{C}$
- VRF** volume reduction factor = $V_{\text{feed}} / V_{\text{retentate}}$
increase yield, decrease flux

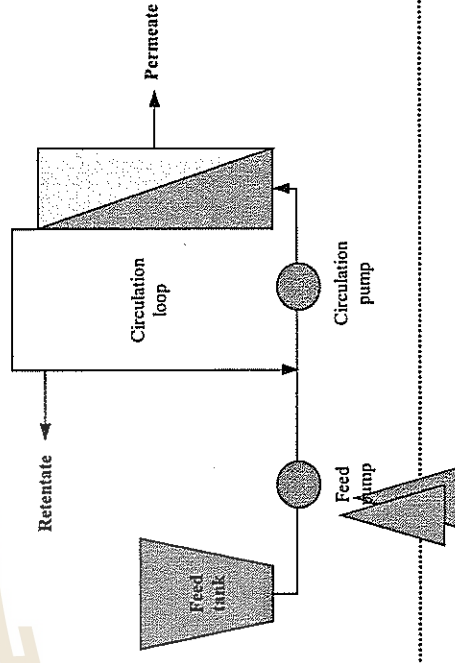
TMP and VRF to be optimized for all new juice / membrane combination
 \Rightarrow high flux (avoid fouling)
 \Rightarrow good retention

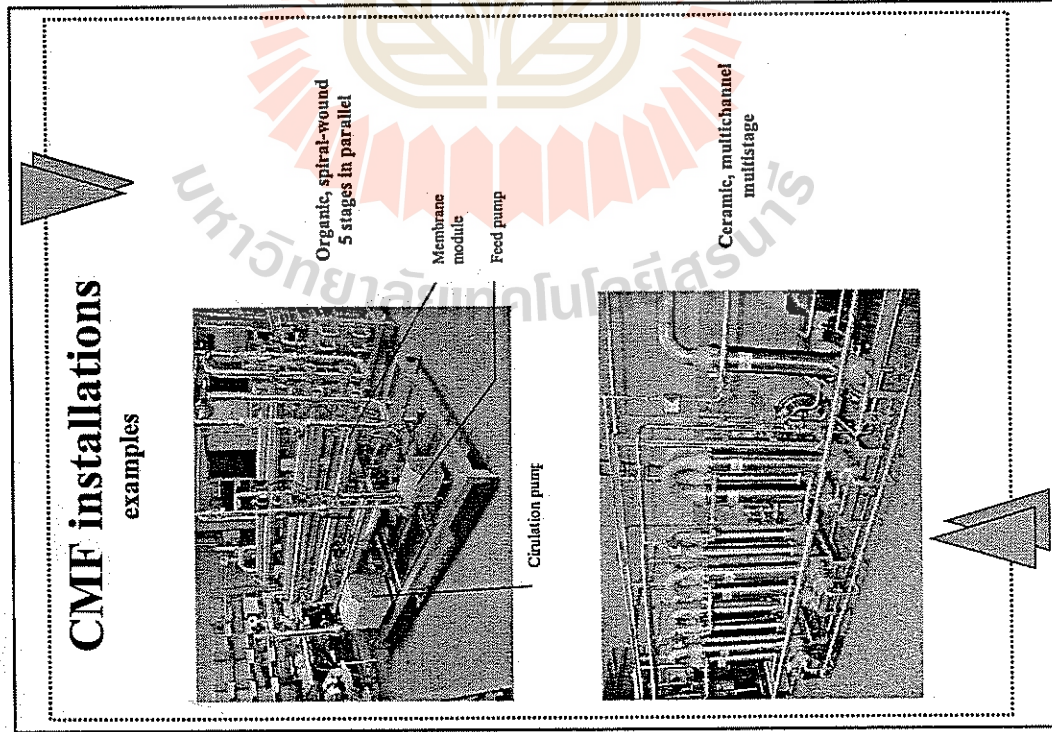
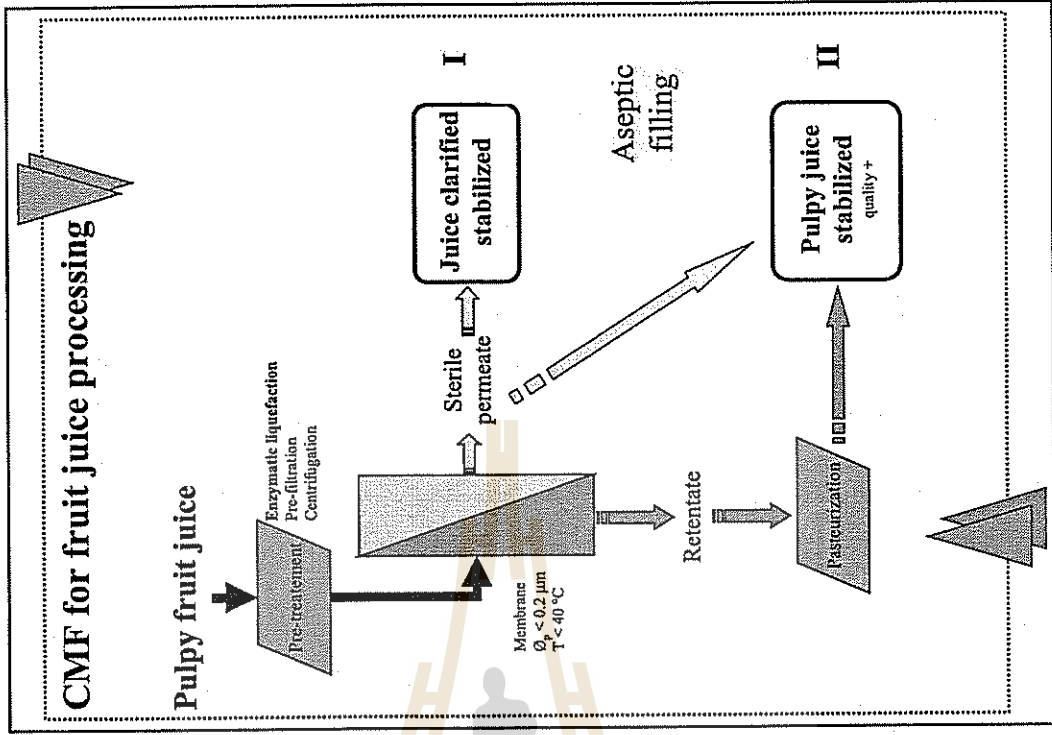
CMF configurations

Batch type with full recycle of retentate



Continuous feed-and-bleed





Way I: clarification of fruit juices using CMF

➤ Clarified juices

- Traditional products: grape, apple, etc.
- New products: tropical fruit juices
 - blending, formulation
 - pre-treatment before RO, resins, etc.

➤ Comparison of clarifying processes

Process	Criteria	Operating time	Clarification efficiency	Sensorial, nutritional quality	Operating cost
Decantation		Very long	Poor	Poor (oxidation)	Intermediate (fining agent)
Dead-end filtration		Long	High	Intermediate	Intermediate (batch process)
Centrifugation		Very short	Poor	High	High
CMF		Short	High	High (+ sterilized)	Low

CMF process optimization

Criteria to be considered

Criteria	Consequence	Target
Permeate flux J_p	Investment cost	To be maximized $> 50 \text{ L h}^{-1} \text{ m}^2$
Retention	Permeate quality	
Insoluble solids	Turbidity	Maximized retention $TU < 5 \text{ NTU}$
Microorganisms	Sterility	Total retention
Soluble compounds	Sensorial quality (colour, flavour)	Minimized retention
	Nutritional quality (vitamins)	Quality near fresh fruit
Operating costs (energy, labour, intrans, cleaning, etc.)	Price of the final product	To be minimized Price \leq juices clarified using traditional methods

CMF process optimization

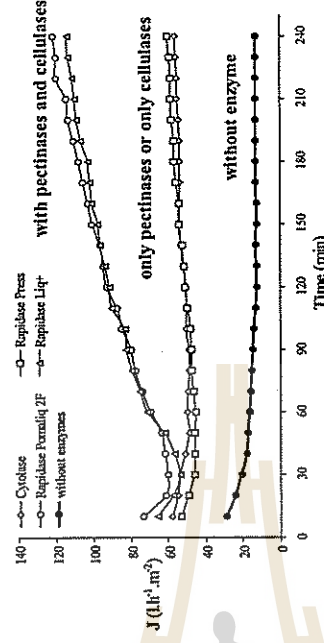
Control parameters

Parameter	Main impact
Enzymatic pretreatment (enzymes, concentration, time, temperature)	J_p (fouling), quality, operating cost (enzymes)
Membrane	J_p , quality, investment cost
Operating conditions	
U	J_p (fouling), operating cost (energy)
T	J_p (viscosity), quality, operating cost (energy)
TMP	J_p (fouling)
VRF	J_p (fouling), operating cost (yield), quality

- Results often difficult to predict
- Experimental approach necessary for each new application

Enzymatic pre-treatment

➤ Examples of experimental results (ceramic memb. 0.2 μm)



Clarification of passionfruit juice
 effect of enzymatic preparation added at 1 ml^l on permeate flux (J)
 (T = 35 °C, TMP = 150 kPa, U = 7 m.s⁻¹, VRF = 1).

- Trends
- Synergistic effect between pectinases and cellulases activities on flux
 - Enz. concentrations high (higher for acidic juices)
 - Duration < 1 h (quality)
 - T < 40 °C to preserve juice quality

TMP optimization

➤ All is possible

➤ Trends

- No prevision possible
- TMP_{opt} not only correlated with insoluble solids content
- Low TMP often better for high flux

VRF optimization

➤ Examples of experimental results (ceramic memb. 0.2 μm)

Clarification of passionfruit and mango juices
effect of volumetric reduction factor (VRF) on permeate flux (J)
after enzymatic treatment (T = 35 °C, $TMP = 150 kPa$, U = 7 $m.s^{-1}$).

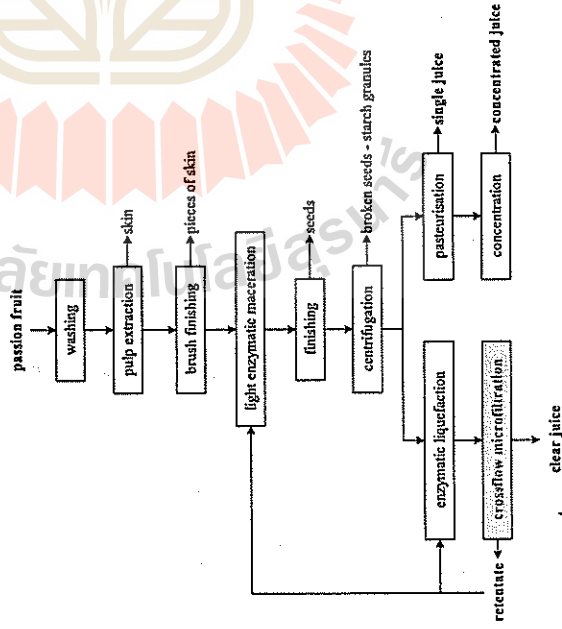
Main results of fully continuous processing carried out on different pulpy fruit juices after enzymatic treatment (T = 35 °C, $TMP = 150 kPa$, U = 7 $m.s^{-1}$).

Fruit juice	Optimal VRF	Jp during retentate removal ($l.h^{-1}.m^{-2}$)	Jr to keep VRF constant ($l.h^{-1}.m^{-2}$)
Tangerine	3.5	50	20
Pineapple	3.5	70	28
Narunjilla	3.2	65	30
Passionfruit	3.0	40	20
Castillas blackberry	3.0	70	35
Mango	1.3	60	200

VRF optimization

> Trends

- High VRF (> 10) easy to reach with juices with low pulp content (grape, apple)
- For very pulpy juices (tropical fruits), low VRF_{opt} (< 5) ⇒ low yield (1-1/VRF) ⇒ necessity to valorize the retentate by re-introducing the retentate into the processing line



Typical flow sheet for simultaneous production of clarified and whole passion fruit juices.

Examples of optimum conditions

Laboratory or pilot plant scale

Juice	Memb.	TMP (bar)	U (ms ⁻¹)	T (°C)	VRF	Perm. Flux (L·h ⁻¹ ·m ⁻²)	Source
Apple	Tubular ceramic 0.1 µm	4.1	8	50	10	160-190	Fukumoto 1998
Orange, lemon	Tubular ceramic 0.5-0.8 µm	0.5-4.0	0.5-12	20-40	1	10-60	Caparelli 1994
Tangerine	Plate & frame polysulfon. 0.1-0.2 µm	0.9-1.9	1-3.5	25	1	40-70	Chamchong 1991
Pine-apple	Tubular ceramic 0.2 µm	1-5	1-4	30	1-3	52-60	Jaeger 1998 Itoua 1991
Apricot	Tubular ceramic 0.45 µm	2	3	50	1	80	Hartet 1989
Manguo	Tubular ceramic 0.2 µm	1	4	20	5	55	Olte 1997
Passion fruit	Tubular ceramic 0.2 µm	1.5	7	36	3	50	Vaillant 1999

Product quality

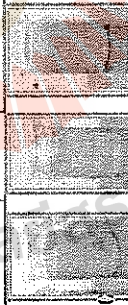
Examples of experimental results (ceramic memb. 0.2 µm)

Main chemical and physical characteristics of different products during passionfruit juice processing using CMF

	Raw juice	Enz. treated juice	Clarified juice	Retentate at VRF = 3
Soluble solids (g.kg ⁻¹)	140 (8)	148 (10)	130 (8)	150 (10)
Suspended solids (g.kg ⁻¹)	254 (10)	148 (5)	< 1	294 (10)
Titrate acidity (g citric ac.kg ⁻¹)	42 (1)	42 (1)	42 (1)	43 (1)
pH	2.9 (0.1)	2.9 (0.1)	3.0 (0.1)	3.0 (0.1)
Glucose (g.l ⁻¹)	26 (2)	34 (2)	31 (2)	33 (2)
Fructose (g.l ⁻¹)	14 (1)	19 (1)	18 (1)	19 (1)
Sucrose (g.l ⁻¹)	5 (1)	6 (1)	6 (1)	5 (1)
Galacturonic acid (g.l ⁻¹)	1.4 (0.1)	1.4 (0.1)	1.4 (0.1)	1.7 (0.1)
Alcohol insoluble solids (g.kg ⁻¹)	0.85 (0.05)	0.06 (0.05)	< 0.01	1.70 (0.06)
Density (kg.m ⁻³)	1027 (2)	1027 (2)	1026 (2)	1027 (2)
Viscosity at 20 °C (mPa.s)	15 (1)	8 (1)	1 (0.1)	6 (1.5)

Standard deviation from 3 or 4 experiments

- High clarification rate
- Sterilization effective if $\Delta p < 0.1$ bar
- Weak retention of soluble compounds
- Vitamin C losses < 10 %
- Little decrease of aromatic strength



Clarification of fruit juices using CMF

Conclusions

- Experimental tests on pilot plant necessary for each new application (optimization)
- Good sensorial and nutritional quality of the clarified juices
- « Cold sterilized » products (aseptic packaging)
- Inorganic membranes often chosen
- Permeate flux between 50 and 100 L h⁻¹ m⁻²
- For very pulpy fruit juices, valorization of retentate necessary for economic viability of the process (recycling or direct use)

Way II : stabilisation of pulpy fruit juices using CMF

- **Objective :** production of pulpy juices stabilized microbiologically
- **Principle :** mix sterile permeate with retentate (that contains microorganisms) after thermic pasteurization + aseptic packaging
- **Advantage :** only a little fraction of the juice (retentate) is submitted to high temperature ⇒ risks of quality alteration limited
- **Optimization schedule :**
 - The lower the quantity of retentate to be pasteurized, the better the quality of the final product
 - ⇒ fraction of retentate = $100 / \text{VRF} (\%)$
 - ⇒ VRF to be maximized
 - Like previously, Jp to be maximized
- **Main results :**
 - Product quality better than whole pasteurized fruit juices
 - Difficulty to reach good Jp with high VRF for very pulpy juices

High interest for juices with high aromatic potential and high vitamin content but the process is being studied to improve flux at high VRF

Conclusions about fruit juice processing using CMF

- Very interesting alternative to produce new high quality products
 - clarified juices
 - pulpy juices stabilized with quality nearer of fresh fruit
- **Difficulty to treat very pulpy juices**
 - pre-treatment necessary (enzymatic)
 - low performance
- **A lot of research works to improve flux**
 - pre-treatment
 - turbulence promotion
 - pulsed back-wash
 - etc.

Concentration using osmotic evaporation

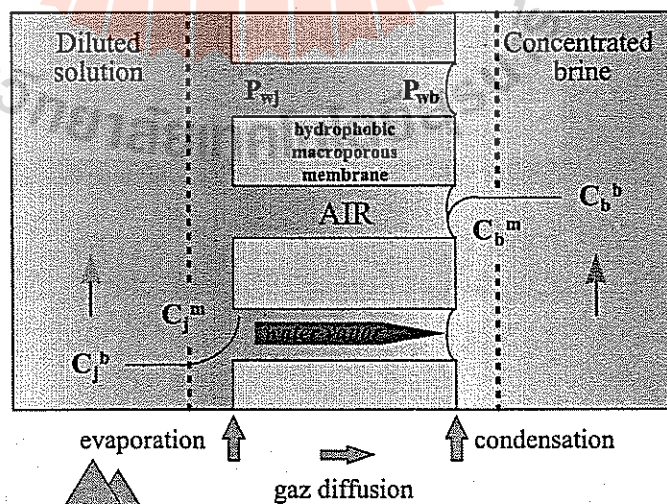
Context

- **Economical aspects**
 - 80 % of fruit juices commercialized as concentrates
 - concentrate = main form of storage and transport
- **Why to concentrate fruit juices ?**
 - decrease mass and volume 5 to 6 times
 - increase product stability (high TSS)

Classical Techniques

Process	Concentration level	Concentrate quality	Cost
Vacuum evaporation	High 50-70 °B	Thermal degradations Aroma losses	High
Cryoconcentration	Low 30-40 °B	High	High
Reverse osmosis	Low 30-40 °B	High	Low

Principle of osmotic evaporation



Interests of the process

- No difficulty to reach high TSS
⇒ **high concentration level**
- Ambient temperature: no thermal degradations
- Total retention of non-volatile solutes
- Losses of volatiles limited
⇒ **high quality concentrates**
- Atmospheric pressure / easy to drive
⇒ **moderated cost**
- Easy to change treatment capacity
⇒ **modulability**

The membrane

- **Material**
hydrophobic polymer ($\sigma < 30 \text{ mN.m}^{-1}$) unwettable by aqueous solutions : PTFE, PVDF, PP, PE
 - **Structural characteristics**
 $0.01 \mu\text{m} < \varnothing_{\text{pore}} < 1.0 \mu\text{m}$
 $50 \% < \text{porosity} < 80 \%$
 $10 \mu\text{m} < \delta < 800 \mu\text{m}$
- ⇒ **classical membrane for air treatment or organic solvents filtration**

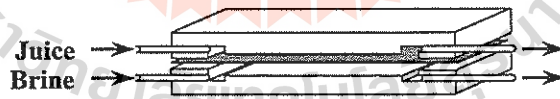
The concentrated brine

- Low water activity ($a_w \ll 0.8$)
 - high soluble salt
 - multivalent salt
- No toxicity
- Moderate cost

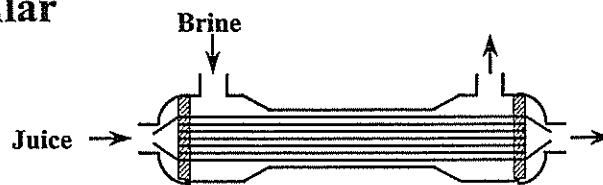
⇒ CaCl_2 5.5 mol.l⁻¹ (45.5 % w/w)

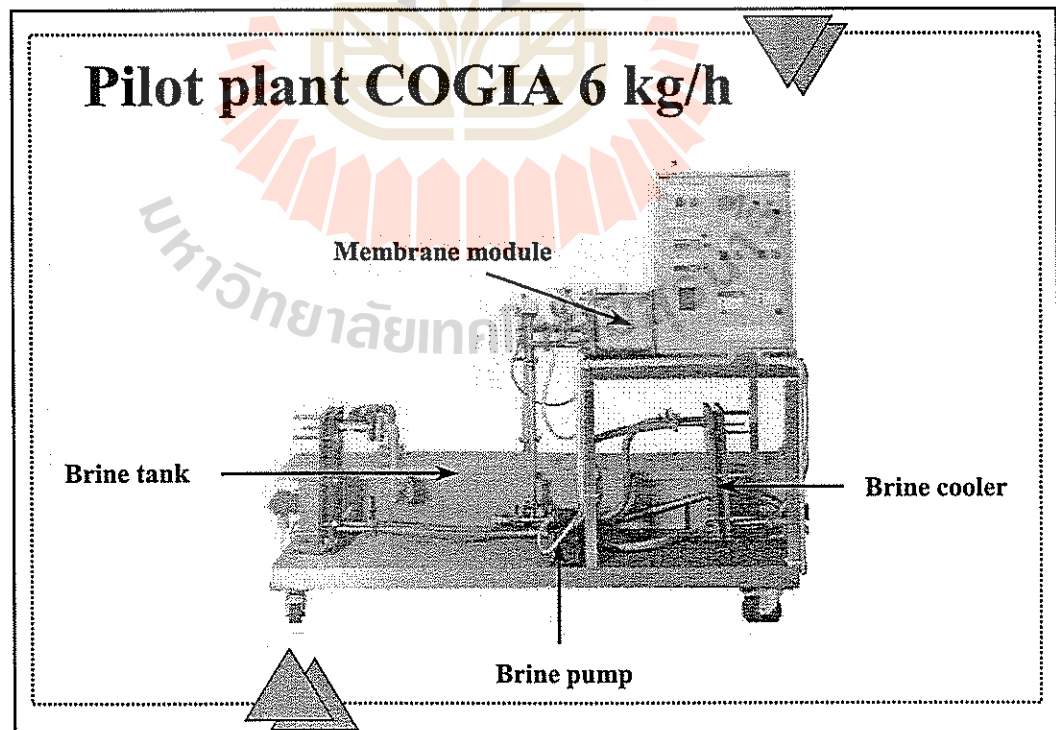
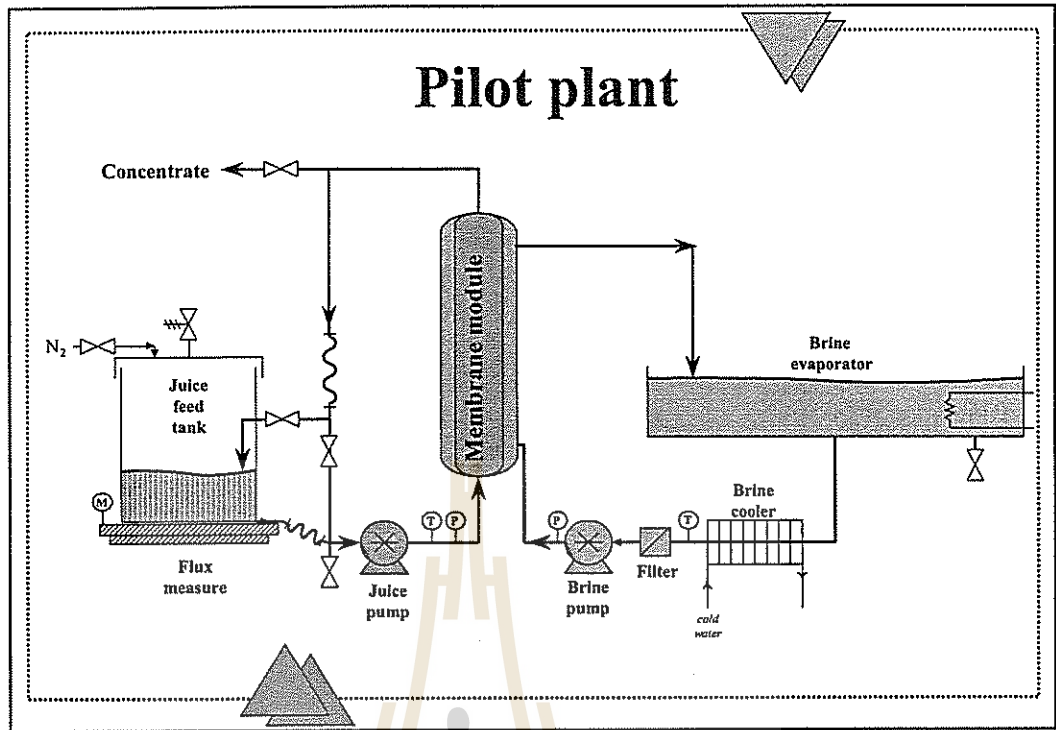
Modules geometry

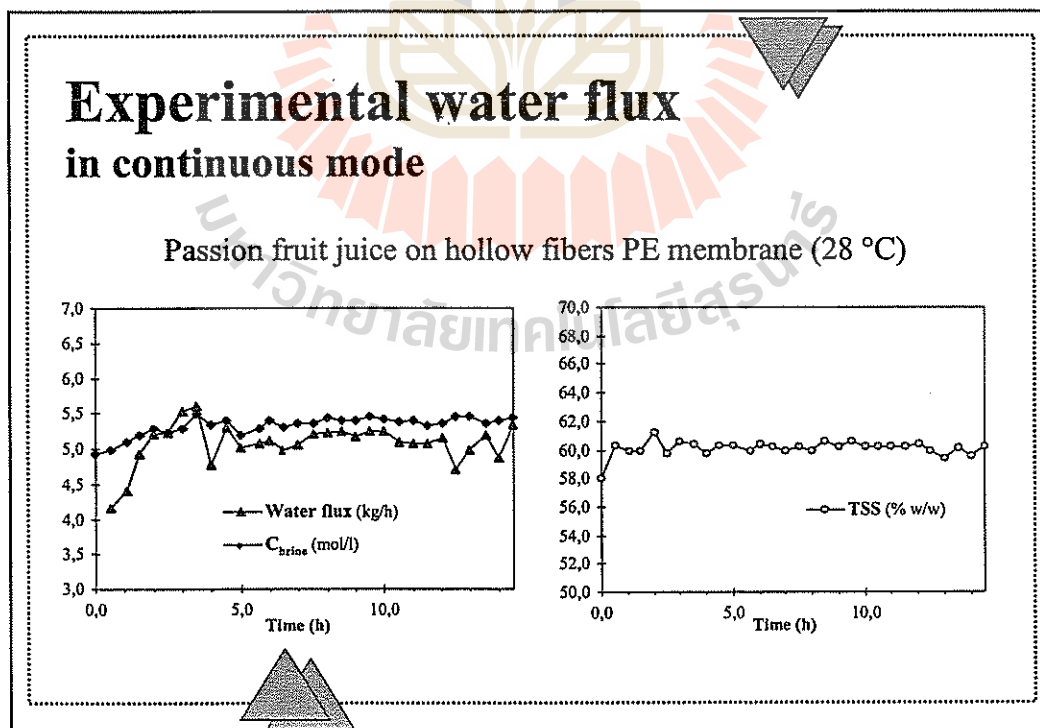
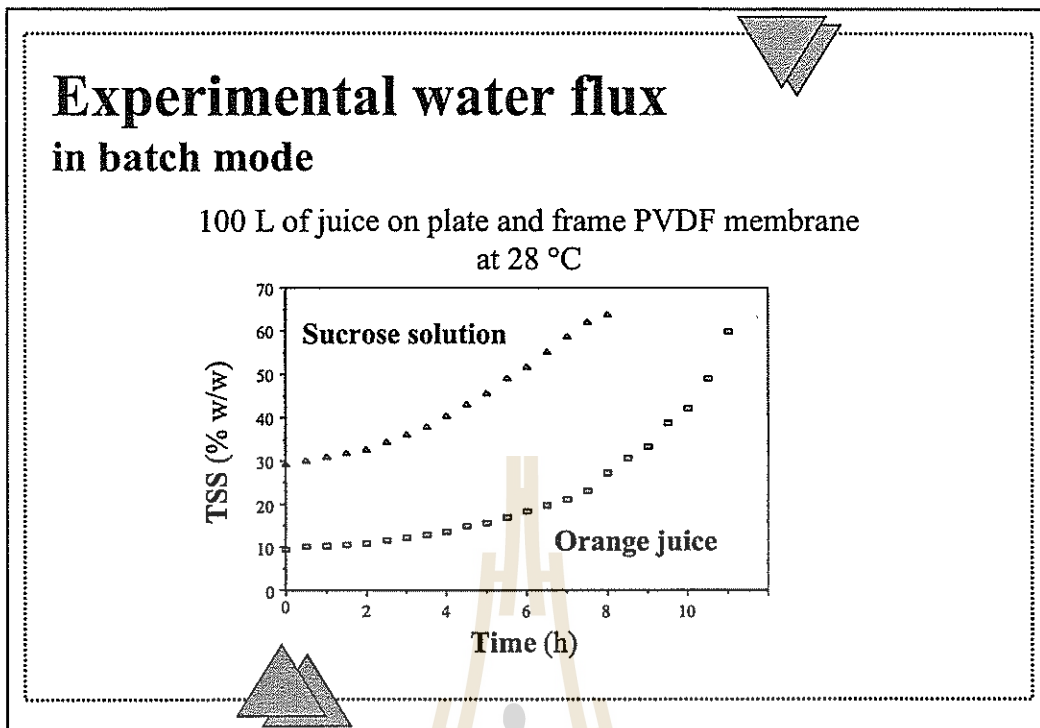
➤ Plane



➤ Tubular







Experimental performances

> Concentration level

- orange juice 60 °B
- whole passion juice 50 °B
- clarified passion juice 65 °B
- pineapple juice 65 °B

> Water flux

$$0.4 \text{ kg.h}^{-1}.\text{m}^{-2} < J_w < 20 \text{ kg.h}^{-1}.\text{m}^{-2}$$

Quality of concentrates

non volatile solutes in orange juice

	Fresh juice	Concentrate
TSS (% w/w)	13.5	60.0
Acidity (g/TSSkg)	0.89	0.89
Sucrose (g/TSSkg)	3.3	3.3
Glu+Fru (g/TSSkg)	3.3	3.4
Vit. C (mg/TSSkg)	24	22

Quality of concentrates non volatile solutes in passionfruit juice

Characteristic	Unit	Initial juice	OE concentrate	Thermal concentrate
Total soluble solids (TSS)	g/100 g	14	60	49
pH (20 °C)		3.1	2.8	2.7
Vitamin C	mg/100 mL	11.4	60	5.3
	mg/kg TSS	781	769	86
Titrateable acidity	meq/100 mL	59	350	260
	eq/kg TSS	4.0	4.5	4.2
Water activity (25 °C)		0.99	0.81	0.90
Viscosity (25 °C)	mPa.s	1.3	1500	32
Density	kg m ⁻³	1043	1300	1255

Quality of concentrates volatiles in passionfruit juice

LOSSES (%)	Concentrate* 45 °B osmotic evaporation	Concentrate 41 °B vacuum evaporation
Limonen	< 1	93
Ocimen	< 1	97
Myrcen	< 1	96
Ethyl acetate	37	96
Ethyl butanoate	52	96

pretreated by CMF.

Quality of concentrates

sensorial analysis of passionfruit juice

Triangular test

No significant difference between fresh and concentrated juice (after redilution)

Hedonic tests

Colour, taste, aroma

Sensorial profile of the juice concentrated using OE nearer of fresh fruit than those concentrated using vacuum evaporation

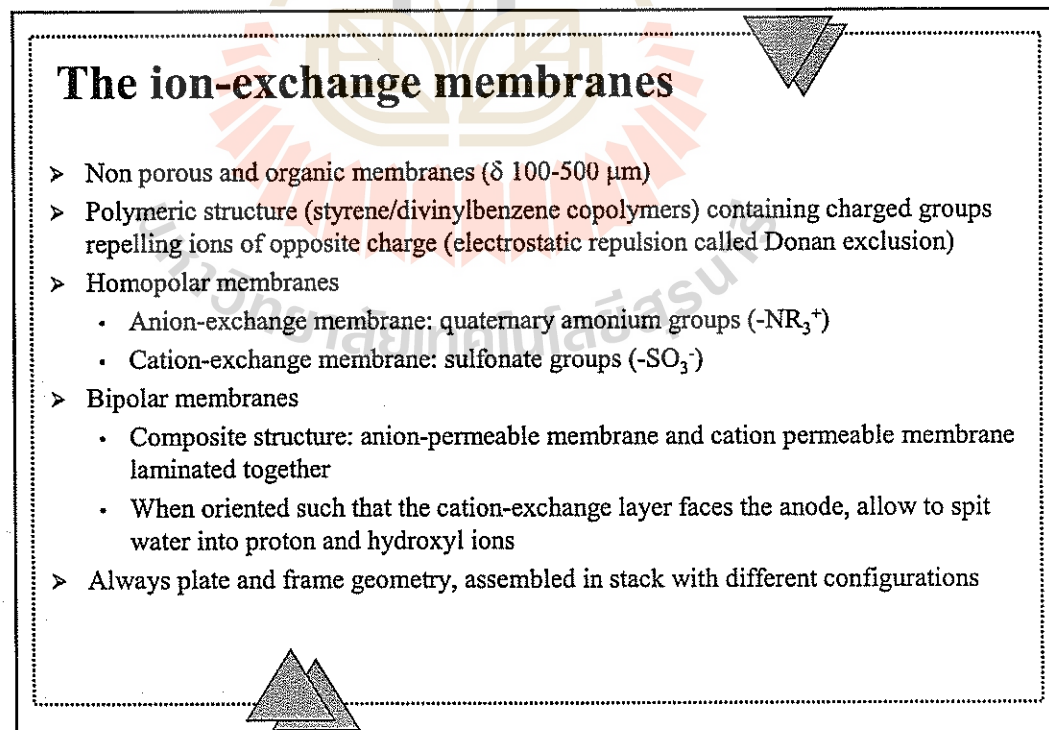
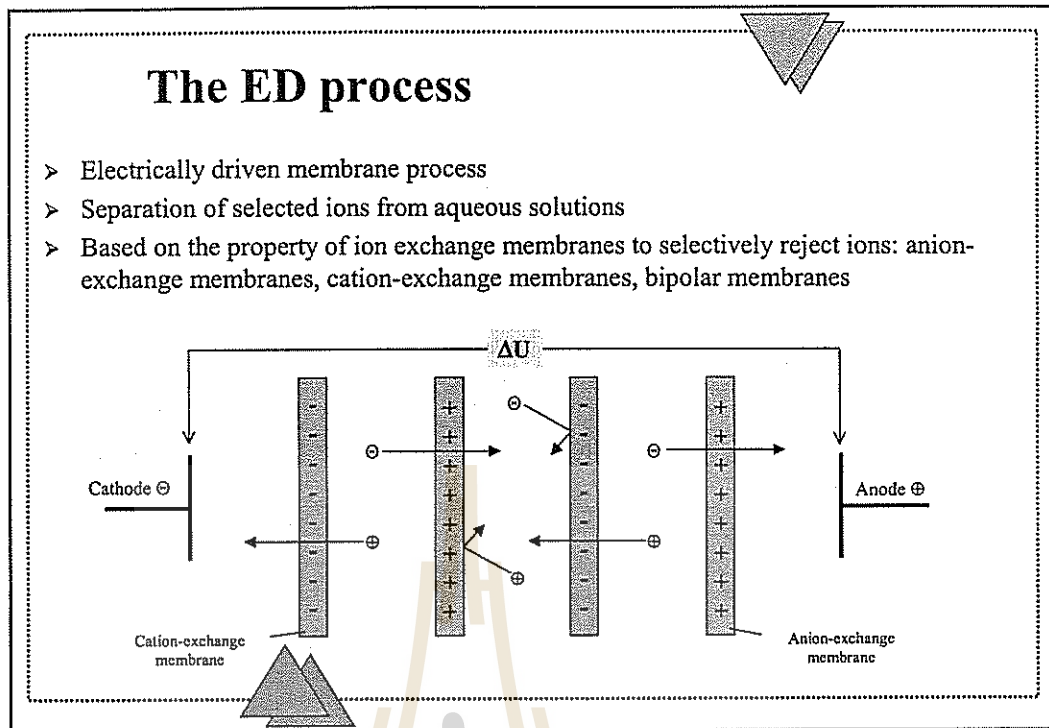
Conclusion

- Osmotic evaporation allows to
 - concentrate fruit juices up to 65 °B
 - better preserve juice quality
 - nutritional (vitamins)
 - sensorial (colour, flavour)
- A promising membrane technique for the production of concentrates with high quality
- A process to be optimized for industrial scale

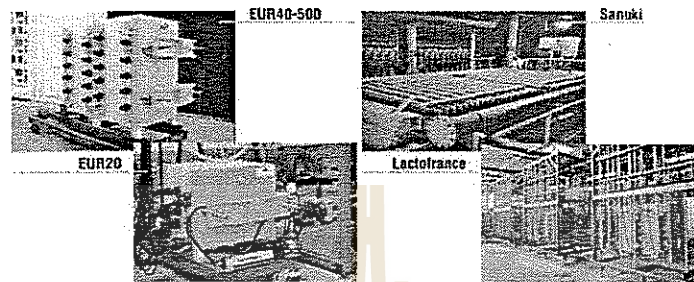
Main research works

- Optimization of membrane/module configuration and operating conditions
- Better control of volatiles transferts
- Association with other membrane techniques (CMF, RO)

Deacidification using electrodialysis



Examples of industrial ED installations



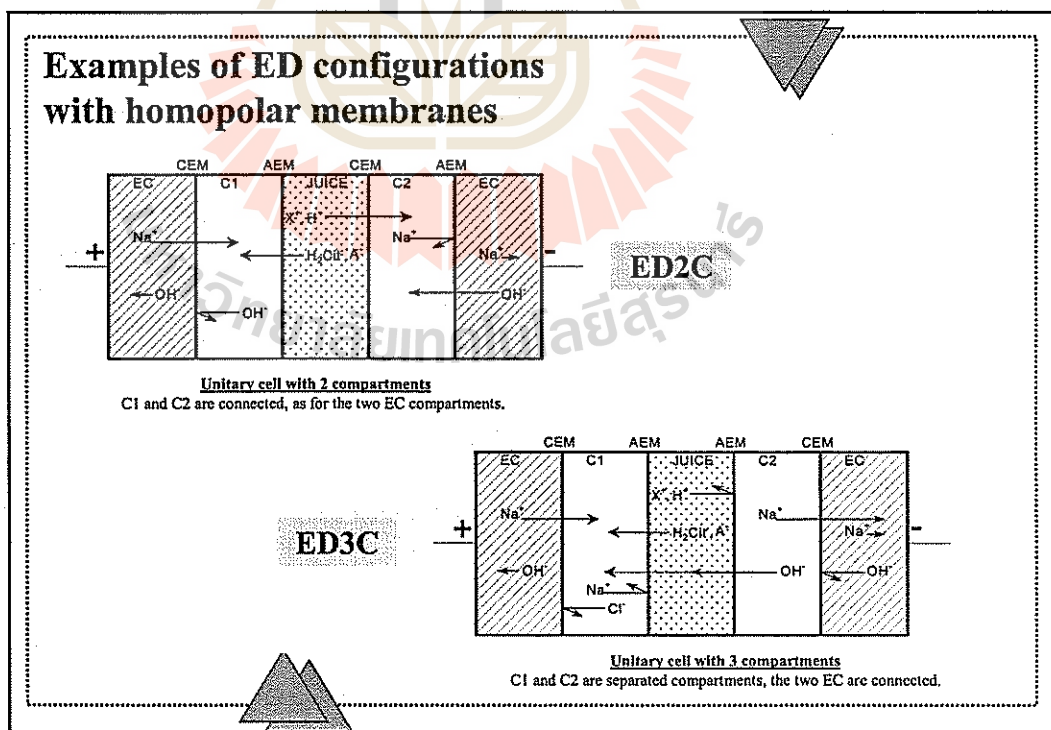
Why deacidify fruit juices ?

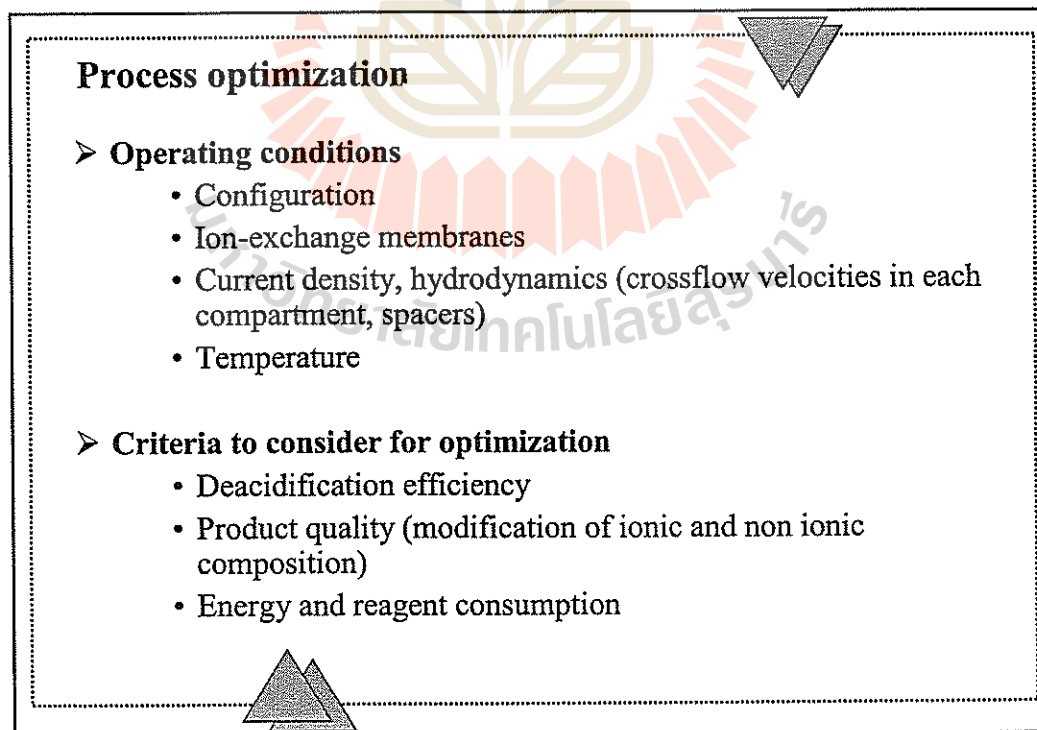
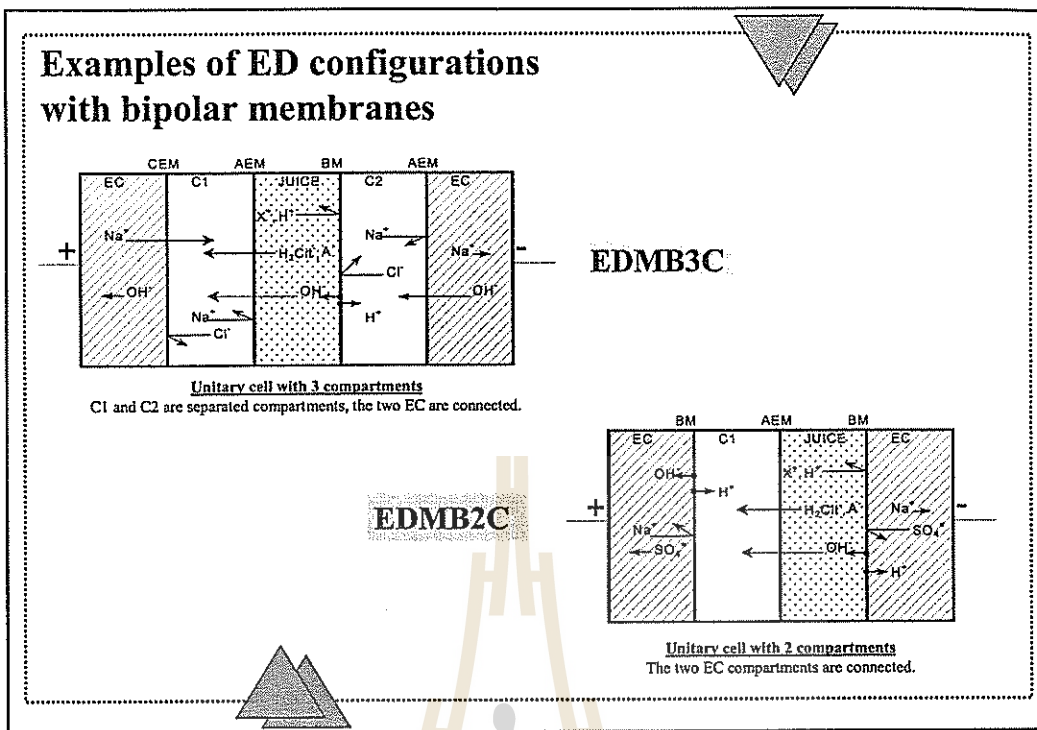
- Very acidic juices: passionfruit, lemon, castillas blackberry, etc. (pH 2,5 – 3,0)
- High acidity limits uses as ingredients in the formulation of various preparations (beverages, ice-cream, etc.)
- Purpose: decrease acidity (up to $\text{pH}_{\text{final}} \approx 4$) with gentle effect on aromatic quality of juice

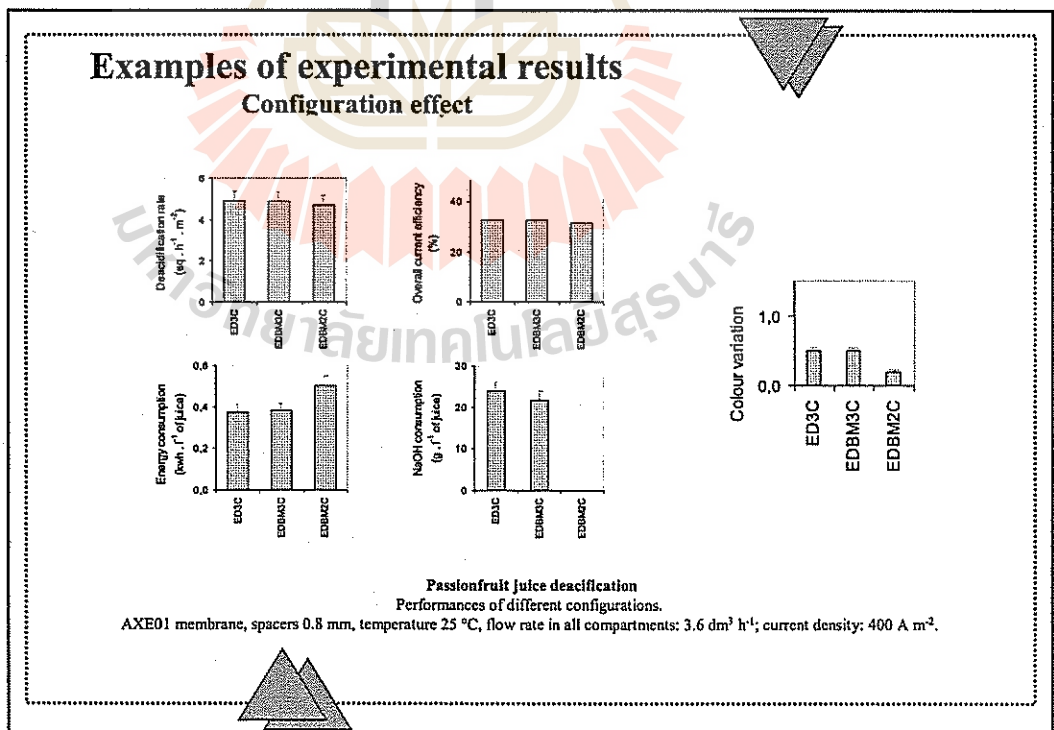
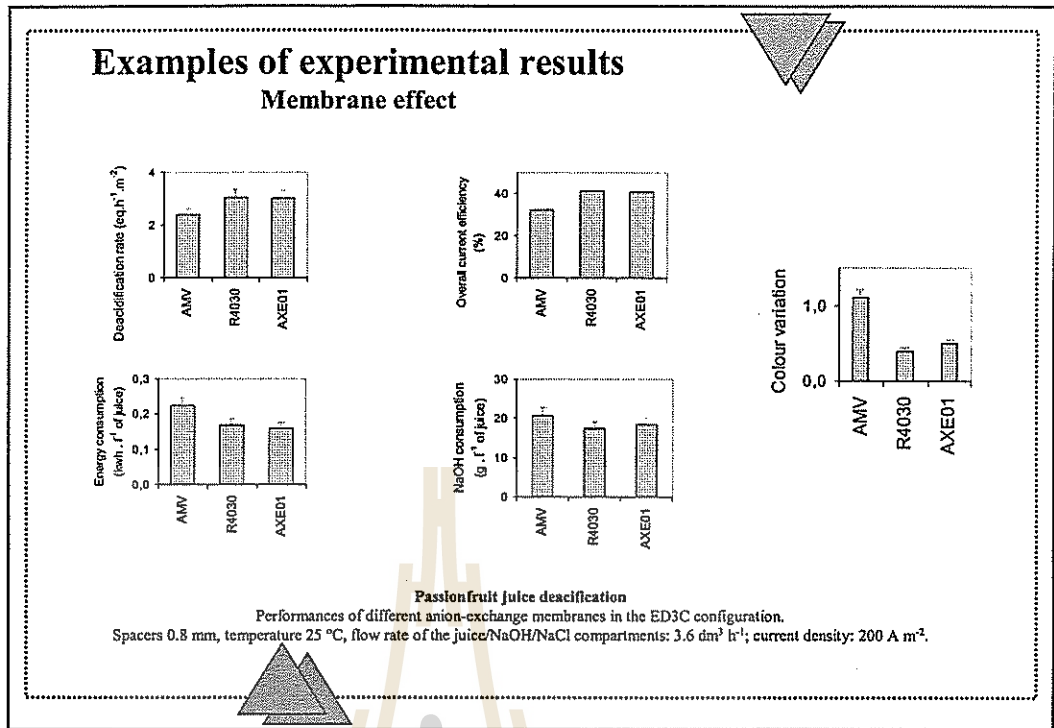
Available processes

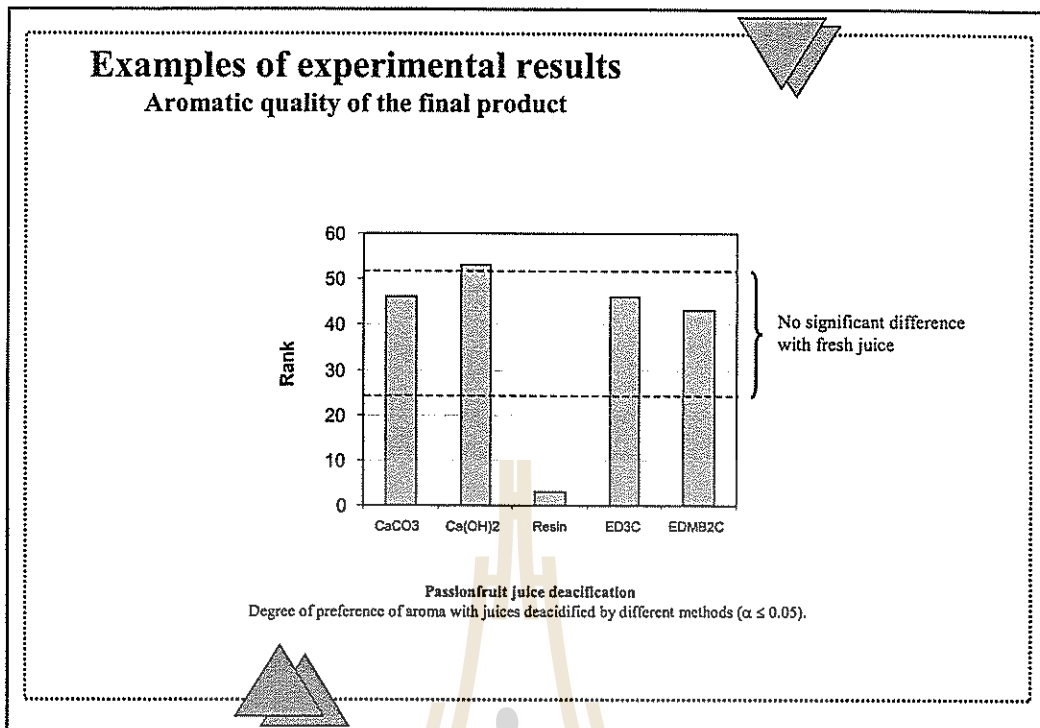
	Type	Product quality	Invest. cost	Operating cost	Wastes production	Other drawbacks
Neutralization by soda	Batch	A lot of flavour modifications	-	--	No	Marketing problem: not natural product (addition of reagent)
Precipitation as Ca salts (citrate, tartrate, malate)	Batch	Good	-	-	Precipitation muds	
Ion-exchange resins	Batch	Flavour and colour modifications (adsorption)	+	+ (chemical for regeneration)	Regeneration effluents	Pre-clarification necessary

Find other process: continuous, without wastes production, « natural product » image, aromatic quality clother than fresh fruit, cost compatible with the market requirements









- ### Conclusion
- Electrodialysis allows to
 - deacidify acidic juices up to pH 4
 - without generating wastes
 - without adding chemical reagent into the product
 - preserve better juice quality than ion-exchange resins
 - A good alternative to develop new low-acidic juices with high aromatic quality
 - A process to be evaluated economically for industrial applications

General conclusions

> Interests of the membrane techniques presented

	Increase quality	New products
Microfiltration	Pulpy juices reconstituted (perm. + pasteuriz. ret.)	Clarified juices stabilized at low T
Osmotique evaporation	« cold » concentrates	
Electrodialysis		Aromatic juices deacidified

> Processes with high potential when compared with classical techniques

> Industrial evaluation in progress (CFM, OE)

- ✓ Optimization in order to increase performances
- ✓ Impact on nutritional and sensorial quality must be studied more thoroughly
- ✓ A lot of research works on membrane materials and other membrane processes